S/079/62/032/010/006/008
D204/D307

AUTHORS: Kabachnik, M.I., Chang, Jung-Yü, and Tsvetkov, Ye.N.

TITLE: The esters of unsaturated phosphinous acids

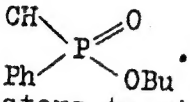
PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 10, 1962, 3351 - 3360

TEXT: The above class of compounds was studied in view of its potential applications to synthesis. Esters of the vinyl-, ethinyl-, allyl-, p-styryl- and of vinyl phenyl phosphinous acids $RP(OR')_2$, were prepared by the reaction of Grignard reagents RMgX with ClP $(OR')_2$, at -60°C, in the presence of pyridine. The butyl esters of vinyl, -methyl vinyl, - ethyl vinyl, - butyl vinyl, - allyl vinyl, - and diallyl phosphinic acids were prepared by the Arbuzov rearrangement of the corresponding butyl phosphinites, using high boiling alkyl halides. The reactions were carried out in toluene, at atmospheric pressure. Vinyl, allyl, and vinyl phenyl - phosphinous esters were readily oxidized, with activated MnO_2, to $CH_2 = CHP(O)$

Card 1/2

The esters of unsaturated ...

$(OBu)_2$, $CH_2 = CH.CH_2P(O)(OBu)_2$ and

$CH_2 =$  . Sulphur was added to the vinyl and allyl phosphinous esters to give the corresponding thiophosphinates. Vinyl, -ethinyl, - and allyl- phosphinous esters underwent acid hydrolysis to $RP(O)HOR'$, whilst phenyl vinyl phosphinous acid could not be liberated by the hydrolysis of its ester, owing to polymerization.

$CH_2 = CHP(OBu)_2$ reacted with Cl_2 to give $CH_2 = CHP(O)(Cl)OBu$ and entered into a diene synthesis reaction with cyclopentadiene at $\sim 200^\circ C$. The corresponding monobutyl ester polymerized readily on heating ($100^\circ C$, 5 hrs.) and in the presence of initiators.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 28, 1961

Card 2/2

KABACHNIK, M.I., akademik; TSVETKOV, Ye.N.

"Pseudoallyl" rearrangements of tri-(chloromethyl)-phosphine.
Dokl. AN SSSR 143 no.3:592-595 Mr '62. (MIRA 15:3)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Phosphine)(Radicals(Chemistry))

TSVETKOV, Ye.N.; KABACHNIK, M.I.

Methods of synthesis and analysis of dialkyl thiophosphates and their analogs. Reakts.i.metod.issl.org.soed. 13:267-427 '64.
(MIRA 17:10)

NIKOLAYEV, A.V.; GRIBANOVA, I.N.; YAKOVLEVA, N.I.; DURASOV, V.B.; KHOL'KINA, I.D.; MIRONOVA, Z.N.; TSVETKOV, Ye.N.; KABACHNIK, M.I., akademik

Correlation between the extractive capacity of organophosphorus extraction agents and the σ constants of the substituents at the phosphorus atom. Dokl. AN SSSR 165 no.3:578-581 N '65. (MIRA 18:11)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut neorganicheskoy khimii Sibirskogo otdeleniya AN SSSR.
2. Chlen-korrespondent AN SSSR (for Nikolayev).

ACC NR: AP6030554 SOURCE CODE: UR/0413/66/000/016/0032/0032

INVENTOR: Kabachnik, M. I.; Nikolayev, A. V.; Mironova, Z. N.; Tsvetkov, Ye. N.

ORG: none

TITLE: Preparation of dialkyl(acetoxymethyl)phosphines. Class 12, No. 184848. [announced by Institute of Heteroorganic Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy AN SSSR)]

SOURCE: Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki, no. 16, 1966, 32

TOPIC TAGS: dialkyl acetoxymethylphosphine, triacetoxyphosphine, alkyl halide, ACETONE, ORGANIC PHOSPHORUS COMPOUND

ABSTRACT: In the proposed method, dialkyl(acetoxymethyl)phosphines are obtained by successive treatment of triacetoxyphosphine with an alkyl halide and aqueous triethylamine, or sodium carbonate solution, or NaOH with subsequent treatment of the alkyldi(acetoxymethyl)phosphine formed with the above products. [WA-50; CBE No. 11]

SUB CODE: 07/ SUBM DATE: 20May65/

Card 1/1 UDC: 547.419.1.07

ACC NR: AP6030555 SOURCE CODE: UR/0413/66/000/016/0032/0032

AUTHOR: Kabachnik, M. I.; Nikolayev, A. V.; Mironova, Z. N.; Tsvetkov, Ye. N.

ORG: none

TITLE: Preparation of triacetoxymethylphosphine. Class 12, No. 184850 [announced by Institute of Heteroorganic Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy AN SSSR)

SOURCE: Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki, no. 16, 1966, 32

TOPIC TAGS: ~~triacetoxymethylphosphine preparation;~~ tramethylphosphinyl chloride, acetic anhydride, chloride, organic phosphorus compound

ABSTRACT: In the proposed method, tri(acetoxymethyl)phosphine is obtained by acetylation of tetramethylphosphonium chloride with acetic anhydride in the presence of an acid catalyst, e.g., H_2SO_4, with subsequent cleavage of the tetra(acetoxymethyl)phosphonium compound formed by treatment with NaOH. [WA-50; CBE No. 11]

SUB CODE: 07/ SUBM DATE: 20May65/

Card 1/1 UDC: 547.419.1.07

ACC NR: AP7010711

SOURCE CODE: UR/0020/66/170/005/1103/1106

AUTHOR: Yakovleva, Ye. A.; Tsvetkov, Ye. N.; Lobanov, D. I.; Kabachnik, M. I. (Academician); Shatenshteyn, A. I.

ORG: Physico-Chemical Institute im. L. Ya. Karpov (Fiziko-khimicheskiy institut); Institute of Hetero-Organic Compounds, AN SSSR (Institut elementoorganicheskikh soyedineniy AN SSSR)

TITLE: Protophilic deuterium exchange of some organic compounds of trivalent phosphorus

SOURCE: AN SSSR. Doklady, v. 170, no. 5, 1966, 1103-1106

TOPIC TAGS: deuterium compound, deuterium, organic phosphorus compound, organic nitrogen compound

SUB CODE: 07

ABSTRACT: The authors consider electron effects in organic compounds of trivalent phosphorus, particularly the quantitative aspects of comparable electron effects of substituents in phosphorus and nitrogen compounds of similar structure. The rate of isotopic hydrogen exchange with a 0.8 *N* solution of *tert*-C_4H_9OK is measured in mixtures of various volumes of diglim and deuterated tertiary butanol at 180°C or with a 0.02 *N* solution of potassium amide in deuterated liquid ammonia at 0 or 25°C in several organic compounds.

Card 1/2

UDC: 547.341

ACC NR: AP7010711

The resultant data show a probability that the smaller differences in exchange rates of aromatic and aliphatic CH bonds in methyldiphenylphosphine than in methyldiphenylamine may be attributed to the higher mobility of hydrogen in the aliphatic CH bonds due to *d*-orbital conjugation, and the increase in mobility of hydrogen in the CH bonds in the ortho position due to the additional inductive effect of the second phenyl radical. This work should serve as a basis for more detailed studies on the kinetics of deuterium removal from substances containing deuterium at a definite position in the molecule. We thank M. I. ARSHINOVA and R. M. GORBATOVA for assistance in this work. Orig. art. has: 2 figures and 2 tables. [JPRS: 40,351]

Card 2/2

ACC NR: AP6032977 SOURCE CODE: UR/0379/66/002/004/0458/0463

AUTHOR: Tsvetkov, Ye. N.; Lobanov, D. I.; Kabachnik, M. I.

ORG: Institute of Organometallic Compounds, Moscow (Institut elementoorganicheskikh soyedineniy)

TITLE: Study of the electronic influence of the diphenylphosphino group

SOURCE: Teoreticheskaya i eksperimental'naya khimiya, v. 2, no. 4, 1966, 458-463

TOPIC TAGS: substituent, conjugate bond system, dissociation constant, benzoic acid

ABSTRACT: In order to determine the nature of the electron-acceptor effect of the diphenylphosphino group and elucidate the role of p-π conjugation in the overall influence of the substituent, the authors determined Hammett's constant σ_m of diphenylphosphino and certain other related groups. To this end, meta-substituted benzoic acids containing diphenylphosphino, diphenylamino, diphenylphosphinyl and thiophosphinyl groups were synthesized, and their ionization constants pK_a were measured. It was found that the diphenylphosphino group is not only an electron acceptor, but also a meta-orienting substituent having an unshared electron pair. This is probably due to two causes: (1) lack or weakness of the effect of p-π conjugation and (2) substantial role of the electron-acceptor effect, which is probably due to d_π-p_π conjugation. The diphenylphosphinyl and diphenylthiophosphinyl groups are strong meta-orientants

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ACC NR: AP6032977

with an appreciable contribution of conjugation to the overall effect of the substituent ($\sigma_p - \sigma_m$ is respectively 0.15 and 0.16). A linear Bronsted relationship was observed between the pK_a values of the acids in aqueous alcohol solutions.

SUB CODE: 07/ SUBM DATE: 10May66/ ORIG REF: 003/ OTH REF: 019

Card 2/2

KABACHNIK, M.I.; BALUYEVA, G.A.; MEDVED', T.Ya.; TSVETKOV, Ye.N.; CHZHAN ZHUN-YUY [Chang Jung-ju]

Kinetics and mechanism of bromination of vinylphosphinic acid derivatives. Kin. i kat. 6 no.2:212-220 Mr-Ap '65. (MIRA 18:7)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

L 7898-66 EWT(m)/EPF(c)/EWP(j) RM

ACC NR: AP5024972 SOURCE CODE: UR/0286/65/000/016/0034/0034

AUTHORS: Kabachnik, M. I.; Tsvetkov, Ye. N.; Lobanov, D. I.; Borisov, G.; Malevannaya, R. A.

ORG: none

TITLE: Method for obtaining methyl-di-(aryl-oxymethyl)- or methyl-di-(β-alkoxy-ethoxymethyl)-phosphine oxides. Class 12, No. 173765

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 16, 1965, 34

TOPIC TAGS: alkoxy phosphine oxide, phosphorus compound, organic phosphine, hydrocarbon, organic oxide, organic phosphorus compound

ABSTRACT: This Author Certificate presents a method for obtaining oxides of either methyl-di-(aryl-oxymethyl) or methyl-di-(β-alkoxyethoxymethyl)-phosphines. The oxide of methyl-di-(chloromethyl)-phosphine is reacted with sodium phenolate or with sodium alkoxyethylate in an inert solvent such as toluene.

SUB CODE: 07/ SUBM DATE: 20Jul64

nw

Card 1/1 UDC: 547.419.1.07

TSVETKOV, E. N.; [illegible], G.K.; [illegible], D.I.; KABACHNIK, M.I., akademik

Correlation of the dissociation constants of carboxylic acids RCOOH and Taft's σ-constants with the nuclear quadrupole resonance frequencies of halogens in RHal-type compounds. Dokl. AN SSSR 161 no.5:1102-1105 Ap '65. (MIRA 18:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

KABACHNIK, M.I.; TSVETKOV, Ye.N.

Lower dialkyl phosphinous acids (oxides of secondary phosphines) and some of their properties. Izv. AN SSSR. Ser.khim. no.7:1227-1232 Jl '63. (MIRA 16:9)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Phosphinous acid)

OBREZKOV, Valentin Ivanovich; TSVETKOV, Ye.V., kand. tekhn.nauk; BUL'DYAYEV, N.A., tekhn. red.

[Use of computer technology in hydroelectric power plant calculations] Primenenie vychislitel'noi tekhniki v gidroenergeticheskikh raschetakh. Moskva, Gosenergoizdat, 1963. 215 p. (MIRA 16:10)

(Hydroelectric power stations)
(Electronic computers)

GORNSHTEYN, V.M. (Moskva); GORTINSKIY, S M. (Moskva); KARTVELISHVILI, N A (Moskva); MAMIKONYANTS, L.G. (Moskva); MEL'NIKOV, N.A. (Moskva); TIMOFEYEV, D.V. (Moskva); TSVETKOV, Ye.V. (Moskva)

Principal trends in carrying out overall electrification.
Elektrichestvo no.10:77-79 O '61. (MIRA 14:10)
(Electrification)

TSVETKOV, Ye.V. (Moskva)

Algorithm for the solution of three power engineering problems using an electronic digital computer. Izv. AN SSSR. Otd. tekh. nauk. Energ. i avtom. no.1:54-62 Ja-F '62. (MIRA 15:3)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut elektroenergetiki.
(Electric power distribution) (Electronic digital computers)

SIDEL'NIKOV, G.A., inzh.; TSVETKOV, Ye.V., inzh.

Total flow measuring device. Elek. sta. 34 no.6:80 Je '63.
(MIRA 16:9)
(Boilers--Equipment and supplies)

TSVETKOV, Ye.V.

Operational and design problems in regulating river runoff.
Probl. gidroenerg. i vod. khoz. no.1:168-198 '63.
(MIRA 16:12)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut elektroenergetiki.

GROMOVA, V.Ye., inzh. (Moskva); SILAKOV, V.N., inzh. (Moskva); TSVETKOV, Ye.V., kand.tekhn.nauk (Moskva)

Algorithm and program for calculating optimal seasonal conditions of the reservoirs of the Volga and Kama river hydroelectric power station cascades using the "Ural-4." Elektrichestvo no.3: 15-21 Mr '64. (MIRA 17:4)

TSVETKOV, Ye.V. (Moskva)

Use of hydrological forecasts in the composition of charts for dispatcher control of the reservoirs of hydroelectric power stations. Izv.AN SSSR.Otd.tekh.nauk.Energ.i avtom. no.2:18-27 Mr-Ap '62. (MIRA 15:4)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut elektroenergetiki.
(Hydroelectric power stations—Water-supply)

AUTHOR: Tsvetkov, Ye. V. (Moscow) SOV/24-58-8-12/37

TITLE: On Optimum Regimes of Long Term Regulation of Hydro-electric Stations (Optimal'nyye rezhimy gidrostantsiy dlitel'nogo regulirovaniya)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Tekhnicheskikh Nauk, 1958, Nr 8, pp 75-80 (USSR)

ABSTRACT: The problems of regulating the discharge, based on the theory of continuous stochastic processes are mathematically very difficult. Assuming that the continuous stochastic process of discharge is approximately a Markov process with discrete time, the solutions of these problems can be obtained. The author begins by discussing the hydraulic characteristics of the inflow and the criteria for optimum regimes. Then the seasonal regulation of a hydro-electric station is considered. The optimum economic regime defined by Eq.(4), p 77, applies only if conditions of reliability are fulfilled. The possibility of forecasting the discharge over a short time interval is mentioned briefly and there is a concluding note on the optimum regimes for a hydro-electric station in the absence of a clearly expressed regulation

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On Optimum Regimes of Long Term Regulation of Hydro-electric Stations

cycle.
There are 2 figures and 4 references, three of which are Soviet, 1 French.

SUBMITTED: March 5, 1958

1. Power plants--Water supply 2. Power plants--Operation
3. Power plants--Climatic factors 4. Water--Control

APPROVED FOR RELEASE: 04/03/2001 CIA-RDP86-00513R001757220013-3"

TSVETKOV, Ye.V. (Moskva)

Optimum operating modes of hydroelectric and thermal power stations which are under joint year-long control. Izv.AN SSSR.Otd.tekh.nauk. Energ.i avtom. no.3:21-27 '60. (MIRA 13:7)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut elektroenergetiki.
(Hydroelectric power stations)
(Electric power stations)

TSVETKOV, Ye. V.: Master Tech Sci (diss) -- "Optimum water-power conditions of hydro-power stations in complex power systems with deterministic and probabilistic descriptions of the river flow". Moscow, 1959. 17 pp (Min Higher Educ USSR, Moscow Order of Lenin Power Engineering Inst), 150 copies (KL, No 11, 1959, 120)

TSVETKOV, Ye.V. (Moscow)

Optimum conditions for hydroelectric power stations with protracted flow regulation. Izv. AN SSSR. Otd.tekh.nauk no.8:75-80 Ag '58. (MIRA 11:9)

(Hydroelectric power stations) (Hydrodynamics)

TSVETKOV, Ye. V., inzhener.

Method for constructing a zone of excess flow on the dispatch graph of a hydroelectric power plant reservoir. Gidr.stroi. 26 no.6:24-27 Je '57. (MLRA 10:7)

(Hydroelectric power stations)

TSVETKOV, YU. D

AUTHOR RAZUVAYEV, G.A., SOROKIN, YU A., DOMRACHEV, G.A., 20-6-30/59
PETUKHOV, G.G., TSVETKOV, YU. D, MOLIN, YU.N.

TITLE On the structure of organochromic compounds.
(O stroyenii khromorganicheskikh soyedineniy.- Russian)

PERIODICAL Doklady Akademii Nauk SSSR 1957, Vol 113, Nr 6, pp 1293-1294
(U.S.S.R.)

ABSTRACT In a paper recently published by Fischer the synthesis of neutral dibenzolchromium and its salts is described and a report is made concerning some further aromatic derivatives of the chromium-(0). This author assumes that the latter compound has an A-structure analogous to ferrocaen. Recently a series of reports was published in which the separation from the reaction products of C_6H_4MgBr and also of the dibenzolchromium with waterless chlorinechromium beside "pentaphenylchromhydroxide" and "tetra" as well as "triphenylchromiodides" is described by Hein. Acoording to a bold, but not precisely proved assumption of Zeiss, the polyphenyl derivatives of chromium have a common bis-aren-structure. If it is assumed that in the chromium iodides (π-benzol, π-diphenyl) and di-(π-diphenyl)-chromium the diphenylgroups are covalently connected, 10 % of D should be expected in the diphenyl separated after the

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On the structure of organochromic compounds. 20-6-30/59

reaction with $LiAlD_4$. If, however they have a B-structure (illustration 1) diphenyl would contain no deuterium. The composition and the yield of the organic products of the light dispersion of the organochromic compounds in the chloroform agree well with the B-structures. It is known that the compounds of the B-series are paramagnetic and have the magnetic moment = 1.7 of the Bohrs magneton. This corresponds to the existence of a not coupled electron in their molecule. Therefore, the photographing of the spectra of the paramagnetic electron-resonance of such compounds was interesting in order to obtain data about the localisation of the free electron. The absorption spectrum of the aqueous solution of one of these substances (III) is shown by illustration 2. The existence of a superfine structure and the qualitative analysis of the intensity distribution shows that the not coupled electron is in interaction with the hydrogen nuclei of the aromatic rings. (2 illustrations, 1 Slavic reference.)

ASSOCIATION: Scientific Research Institute for Chemistry at the Gorkij State University "N.I. LOBACHEVSKIY".
MOSCOW PHYSICAL'TECHNICAL INSTITUTE.
Institute for Chemical Physics of the Academy of Science of the U.S.S.R.

CARD 2/3

20-6-30/59

On the structure of organochromic compounds.

PRESENTED BY: N.N. SEMENOV, Member of the Academy.
SUBMITTED: 4.3. 1957
AVAILABLE: Library of Congress.

CARD 3/3

TSVETKOV, Yu. D

TSVETKOV, Yu.D.; VOYEVODSKIY, V.V.; RAZUVAYEV, G.A.; SOROKIN, Yu.V.; DOMRACHEV, G.A.

Electron paramagnetic resonance in some sandwich-type chromium aromatic compounds. Dokl. AN SSSR 115 no.1:118-121 Jl-Ag '57. (MIRA 10:11)

1. Institut khimicheskoy fiziki AN SSSR i Gor'kovskiy gosudarstvennyy universitet. Predstavleno akademikom A.N.Nesmeyanovym.
(Chromium organic compounds--Spectra) (Electrons)

AUTHORS: Chernyak, N. Ya., Bubnov, N. N., Voyevodskiy, V. V., Polak, L. S., Tsvetkov, Yu. D. SOV/20-120-2-34/63

TITLE: The Formation of Free Radicals and of Atoms in the Radiolysis of Hydrocarbons at a Temperature of 77°K (Ob obrazovanii svobodnykh radikalov i atomov pri radiolize uglevodorodov pri temperature 77°K)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 2, pp. 346 - 348 (USSR)

ABSTRACT: References are made in publications to free radicals formed during the action of ionizing radiation, as by X-rays, γ-radiation, fast electrons etc. This is caused by a rupture of C - C and of C - H bindings. When fluid hydrocarbons are radiolysed, the life of the free radicals is very short. The main products of radiolysis, apart from liquid products with one or two conjugated double bindings, are H_2 and $C_{14}H_{30}$. The latter compound is considered to be a dimer of the heptyl radical. The method of determining the radical is shortly described. The following hydrocarbons were investigated: hexane,

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heptane, octane, dodecane, cetane, isooctane, cyclohexane, benzene and toluene. In all cases intensive signals of paramagnetic electron resonance with a g-factor of ~ 2,0 are observed. In paraffin-type hydrocarbons and in cyclohexane a hyperfine structure was very clearly observed. According to the attached photographs the hyperfine structure is considerably changed if the structural properties of the initial molecule change. Another peculiarity of the spectra pf paramagnetic electron resonance of the hydrocarbons which are irradiated in a frozen state is the existence of considerable concentrations of hydrogen atoms. This is also indicated by two narrow signals which are located symmetrically at a distance of about 250 Oersted (Ersted) from the signals of the alkyl radical. The hydrogen atoms probably do not become stabilized in the volume of the frozen hydrocarbons but on the internal surface of the quartz ampoule. In a table the quantitative measurements performed on the basis of the example of heptane concerning the concentration of the free radicals with a dose of~ 10^7r are compared with the data of the chemical analysis of a sample irradiated under absolutely identical conditions. The results

The Formation of Free Radicals and of Atoms in the Radiolysis of Hydrocarbons at a Temperature of 77°K SOV/20-120-2-34/63

obtained by both measurements agree in a satisfactory manner. There are 2 figures, 1 table, and 4 references, 2 of which are Soviet.

ASSOCIATION: Institut nefti AN SSSR (Petroleum Institute, AS USSR) Institut khimicheskoy fiziki, AN SSSR (Institute of Chemical Physics AS USSR)

SUBMITTED: January 11, 1958

1. Hydrocarbons--Temperature factors 2. Free radicals --Production 3. Atoms--Production 4. Hydrocarbons --Test results

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SOV/2o-122-6-27/49

5(4)

AUTHORS: Tsvetkov, Yu. D., Bubnov, N. N., Makul'skiy, M. A., Lazurkin, Yu. S., Voyevodskiy, V. V., Corresponding Member, AS USSR

TITLE: The Investigation of the Spectra of the Electron Paramagnetic Resonance of Some Polymers Which Were Irradiated at 77°K (Issledovaniye spektrov e.p.r. nekotorykh polimerov, obluchennykh pri 77°K)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 6, pp 1o53-1o56 (USSR)

ABSTRACT: The authors carried out the above investigation for the purpose of solving several problems connected with the structure and chemical behavior of organic radicals in the solid phase as well as with the mechanism of chemical transformations in solid organic bodies under the influence of ionizing radiation. Polyethylene, polyvinyl chloride, "Teflon" (polyethylene tetrafluoride), polydimethyl siloxane, polyisobutylene, polymethyl methacrylate and natural rubber were investigated. Carrying out of the experiments is described in short. At 77°K a very intensive signal of paramagnetic electron resonance

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The Investigation of the Spectra of the Electron Paramagnetic Resonance of Some Polymers Which Were Irradiated at 77°K

with a g-factor near 2.0036 was observed in all samples. After "thawing" of the sample down to room temperature the signal was in all cases found to change. In some cases, the signal vanished completely as a result of "thawing" (polyisobutylene, polydimethyl siloxane, natural rubber). In the case of other materials the character of the signal and its fine structure changed considerably. A comparison of all data obtained gave the following result: The character of the spectra obtained by investigating not "thawed" samples can be fully explained by the assumption that the predominant primary chemical act in irradiation is the stripping of one of the C-H bonds in the main chain (or in the absence of a main chain the stripping of a C-H bond in a lateral chain). The spectrum of paramagnetic electron resonanne recorded at 77°K consists of 6 components. The even number of the spectrum in this as well as in other cases is connected with the formation of the radical $\sim Ch_2-\dot{C}H-CH_2\sim$. The authors then discuss several details, especially such as concern the investigation of Teflon. By the irradiation of Teflon at low temperatures it is possible

SOV/2o-122-6-27/49

The Investigation of the Spectra of the Electron Paramagnetic Resonance of Some Polymers Which Were Irradiated at 77°K

to obtain materials with fully satisfactory mechanical properties. These substances contain a large quantity (~0.1 %) of free radicals. There are 2 figures and 7 references, 4 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute for Chemical Physics of the Academy of Sciences, USSR)

SUBMITTED: July 24, 1958

Card 3/3

TSVETKOV, Yu.D.; LEBEDEV, Ya.S.; VOYEVODSKIY, V.V.

Free radical reactions in irradiated polytetrafluoroethylene. Part 1: Use of electron resonance (ER) in studying radical conversions and in the determination of the coefficient of diffusion of oxygen in polytetrafluoroethylene. Vysokom. soed. 1 no.10:1519-1525 O '59. (MIRA 13:3)

1. Institut khimicheskoy fiziki AN SSSR.
(Radicals(chemistry)) (Ethylene) (Oxygen)

TSVETKOV, Yu.D.; LEBEDEV, Ya.S.; VOYEVODSKIY, V.V.

Reactions of free radicals in irradiated polytetrafluoroethylene. Part 2: Determination of the rate constants for the reactions $RO_2 \rightarrow R + O_2$ and $R + O_2 \rightarrow RO_2$. Vysokom.soed. 1 no.11:1634-1642 N '59. (MIRA 13:5)

1. Institut khimicheskoy fiziki AN SSSR.
(Radicals (Chemistry) (Ethylene) (Oxygen)

24(7), 21(1) SOV/51-6-4-27/29

AUTHORS: Bubnov, N.N., Voyevodskiy, V.V., Polyak, L.S. and Tsvetkov, Yu. D.

TITLE: Electron Paramagnetic Resonance Spectrum of Hydrogen Atoms Stabilized on Solid Surfaces (O spektrakh elektronnogo paramagnitnogo rezonansa atomov vodoroda, stabilizirovannykh na tverdykh poverkhnostyakh)

PERIODICAL: Optika i Spektroskopiya, 1959, Vol 6, Nr 4, pp 565-566 (USSR)

ABSTRACT: It was reported (Refs 1, 2) that H atoms, formed on γ-irradiation of frozen hydrocarbons and other compounds, can be stabilized on various surfaces. The present paper reports studies of the effect of the nature of the stabilizing surface on the magnitude of h.f.s. splitting of the electron paramagnetic resonance (e.p.r.) spectra of H atoms and the width of the e.p.r. absorption lines. The H atoms were stabilized on quartz, silica gel and molybdenum glass. They were formed by irradiation of these three substances with γ-rays at 77°K. It may be assumed that formation of H atoms is due to rupture of bonds in H_2O molecules adsorbed on these surfaces or rupture of bonds in SiOH groups (Ref 3). The magnitude of h.f.s. splitting in all the three cases was found to be close to 500 oersted which does not differ greatly from splitting in a free H atom (Ref 4). Width of the components of the hydrogen doublet depends strongly on the nature of the surface: on

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Electron Paramagnetic Resonance Spectrum of Hydrogen Atoms Stabilized on Solid Surfaces

quartz it is close to 0.8 oersted (curve 1 in a figure on p 566), on silica gel it is near 2.4 oersted (curve 2) and on molybdenum glass it is 4.5 oersted (curve 3). Since the hyperfine splitting in the e.p.r. spectra of H atoms stabilized on various surfaces is close to the hyperfine splitting of free atoms, the binding of H atoms to these surfaces does not alter greatly the spin density of the unpaired electron in hydrogen. On the other hand, dependence of the width of the hydrogen doublet components on the nature of the stabilizing surface indicates that there is a definite interaction between the unpaired electron and the surface. In view of this the authors suggest further studies of the nature of binding of H atoms to solid surfaces. This is an abridged translation. There is 1 figure and 4 references, 2 of which are Soviet and 2 English.

SUBMITTED: August 29, 1958

24(7), 5(3) SOV/51-6-4-26/29

AUTHORS: Chernyak, N. Ya., Bubnov, N.N., Polyak, L.S., Tsvetkov, Yu. D. and Voyevodskiy, V.V.

TITLE: On Certain Regularities in the Electron Paramagnetic Resonance Spectra of Alkyl Radicals (O nekotorykh zakonomernostyakh v spektrakh elektronnogo paramagnitnogo rezonansa alkil'nykh radikalov)

PERIODICAL: Optika i Spektroskopiya, 1959, Vol 6, Nr 4, pp 564-565 (USSR)

ABSTRACT: In the study of the electron paramagnetic resonance (e.p.r.) spectra of radicals formed on γ-irradiation or frozen hydrocarbons (at 77°K), it was found that the hyperfine structure (h.f.s.) varies with the position of the hydrocarbon in its homologous series. Fig 1 shows the spectra of radicals of normal paraffin hydrocarbons from $C_{11}H_{23}$ to $C_{16}H_{33}$ obtained under conditions described earlier (Ref 1). The samples were of 97-98% purity. Fig 1 shows that h.f.s. of the even ($C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$) and odd ($C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$) hydrocarbons differ considerably. In odd hydrocarbons the h.f.s. is well resolved and the intensities of the central components differ only slightly from one another. In even hydrocarbons the resolution is much poorer and the intensity distribution is close to binomial. In paraffin hydrocarbons from n-C_5 to n-C_{10} the spectra are more complex and more similar to

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On Certain Regularities in the Electron Paramagnetic Resonance Spectra of Alkyl Radicals

one another. Two of them are shown in Fig 2, where curves 1 and 2 represent the e.p.r. spectra of C_6H_{13} and C_7H_{15} respectively. The spectra of radicals of cyclic hydrocarbons (with five or six C atoms, shown in Fig 3) are in many respects similar to the corresponding spectra of the odd and even terms of the series C_{11}-C_{16}. The simplest spectrum is that of cyclo-C_6. The hyperfine splitting and component intensities may be explained by assuming that the spectrum is a triplet (with 37 oersted splitting and 1:2:1 ratio of intensities of the components) and each components of the triplet is split into two lines (20 oersted separation). Such a spectrum occurs in the radical cyclo-C_6H_{11}. Following Ingram (Ref 3) it is assumed here that of four hydrogen atoms in the β-position, the free valence, only two take part in the hyperfine splitting. This produces a triplet. Interaction with a hydrogen atom in the α-position produces the doublet splitting of each triplet component. In the case of cyclo-C_5H_{10} the molecule is almost planar and both hydrogen atoms of the β-groups CH_2 in the radical should be equivalent with respect to free valance and the number of h.f.s. components should increase. The spectra shown in Fig 3 confirm these deductions. The authors conclude by pointing out that the e.p.r. spectra

On Certain Regularities in the Electron Paramagnetic Resonance Spectra of Alkyl Radicals

can be used in molecular structure studies and in chemical analysis. There are 3 figures and 3 references, 2 of which are Soviet and 1 English.

SUBMITTED: August 28, 1958

5(4) SOV/76-33-7-37/40

AUTHORS: Molin, Yu. N., Tsvetkov, Yu. D.

TITLE: On Changes in the Course of the Lines of Electron Paramagnetic Resonance With Temperature in Radicals of the Peroxide Type

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1668 - 1670 (USSR)

ABSTRACT: In the papers (Refs 1,2), the spectra of electron paramagnetic resonance (EPR) of irradiated Teflon were investigated, and it was found that under the influence of oxygen radicals of the peroxide type are formed

$$\sim\sim CF_2 - \underset{\displaystyle O}{\overset{\displaystyle O}{|}}{CF} - CF_2 \sim\sim \quad (2)$$

Furthermore, it was found that the course of the absorption curve of radical (2) depends largely on temperature. In this article, the authors carried out pertinent investigations at -198° ÷ 150° C. Herefrom it resulted that the asymmetry (A) of the above curve does not change within the temperature ranges -200° - -100°C and 50° - 150° C. Within the range -100° - 50°C the course of the curve changes uniformly and (A) changes its sign at about 50° C. Several measurements showed that the above changes in the course of the curve take place in a reversible manner within the temperature range under investigation. It is

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On Changes in the Course of the Lines of Electron Paramagnetic Resonance With Temperature in Radicals of the Peroxide Type

SOV/76-33-7-37/40

therefore assumed that radical (2) does not change its structure within this range. The experimental results obtained may be explained by the assumption that the change in the course with temperature depends on the change of motion of the group -O -O with respect to the C - O bond in radical (2). The authors then give some explanations by means of a simple model under the assumption that at temperatures of above 50°C a free rotation of the -O - O group with respect to the C - O bond takes place. However, these considerations hold only in the first approximation since for a quantitative interpretation of the resultant data the shape and height of the potential barrier for the rotation of the - O - O group must be known. There are 2 figures and 4 references, 1 of which is Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva (Academy of Sciences of the USSR, Institute of Chemical Physics, Moscow)

SUBMITTED: August 28, 1958

Card 2/2

TSVETKOV, Yu.D.; MOLIN, Yu.N.; VOYEVODSKIY, V.V.

Electron resonance spectra of some irradiated polymers.
Vysokom.soed. 1 no.12:1805-1811 D '59. (MIRA 13:5)

1. Institut khimicheskoy kinetiki i goreniya AN SSSR (Sibirskoye otdeleniye).
(Polymers--Spectra)

34898
S/081/62/000/003/089/090
B159/B101

11.2214
15.8160

AUTHORS: Tsvetkov, Yu. D., Lebedev, Ya. S., Voyevodskiy, V. V.

TITLE: Research on the reactions of free radicals in irradiated teflon

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 3, 1962, 645, abstract 3R67 (Tr. Tashkentsk. konferentsii po mirn. ispol'zovaniyu atomn. energii. v. 2, Tashkent, AN UzSSR, 1960, 431-440)

TEXT: The electron paramagnetic resonance spectra of the radicals formed on irradiating teflon, and the diffusion of the gases H_2, O_2, NO into the irradiated teflon were studied. At temperatures of 100-200°C a hyperfine splitting due to the interaction of the unpaired electron with 4 fluorine atoms in the gamma position was observed in the spectrum of the radical $\sim CF_2-\dot{C}F-CF_2\sim$ (Ṙ). The value of this splitting is 3.5 oersteds. On lowering the temperature the lines widen; the transition temperature is 135°C, the width of the line 8 Meps. At ~20°C an expansion of the beta-component of the spectrum Ṙ is observed combined with a first-order phase

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Inst. Chem Physics AS USSR

S/081/62/000/003/089/090
B159/B101

Research on the reactions ...

transition in the teflon crystal lattice. The diffusion coefficients (D) of O_2, H_2, and NO for different temperatures and pressures were determined. A direct dependence of log D on 1/T was found. The effective activation energies of diffusion (kcal/mole) are:
$\varepsilon_g(O_2) = 4.6 \pm 0.5$; $\varepsilon_g(H_2) = 4.3 \pm 0.5$; $\varepsilon_g(NO) = 6.0 \pm 1$.
D decreases with a lowering of pressure. The kinetics of the reactions of $\dot{R}$ with O_2, H_2, and NO on thin (100-250 μ) teflon films (for the elimination of the effects connected with diffusion) was studied. The reaction of $\dot{R} + O_2 \xrightarrow{k_2} RO_2$ proceeds quickly (~ 10 sec). The study of the kinetics of the decomposition $\dot{R}O_2 \xrightarrow{k_1} \dot{R} + O_2$ showed that there exist two steps corresponding to the monomolecular decomposition with different k's. The presence of the two steps is dependent on the reactions $\dot{R}O_2 \xrightarrow{k_1} \dot{R} + O_2$; $\dot{R} + O_2 \xrightarrow{k_2} \dot{R}O_2$; $O_2 \xrightarrow{k_g}$ evacuation. $k_g = \alpha D/d^2$ is the diffusion constant of O_2. At the initial moment a monomolecular

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Research on the reactions ...

decomposition takes place with an effective rate constant k, but at higher degrees of conversion - a quasi-monomolecular reaction with an effective rate constant $k_{(eff)} = k_1 k_g / k_2 n_o = k/Kn_o$ takes place. Results of the calculation: ($k_1 = 10^{-5} v_o \exp(-20000/RT)$ sec^{-1}; $k_2 = 10^{-5} Z_o \exp(-6000/RT)$ cm^{-3}/sec; $\dot{R} + O_2 \underset{}{\overset{k_3}{\rightleftharpoons}} \dot{R}O_2$, $k = 10^{-23} \exp(14000/RT) cm^{-3}$. The kinetics of the process $\dot{R} + H_2 \xrightarrow{k_3}$ are described by the quasi-monomolecular law with

$k_{(eff)} = k_3[H_2]_p = k_3 k_p^{(H_2)} p_{(H_2)}$; $k_3 k_p^{(H_2)} = 50 \exp(-8500/RT)$ sec^{-1}/mm Hg.

The reaction $\dot{R}O_2 + H_2 \xrightarrow{k_4}$ passes through an intermediate stage - the decomposition of the peroxide radical. $E_{(act)} = \sim 20$ kcal/mole. The interaction of $\dot{R}$ with NO leads to the appearance of the spectrum of a new radical $\sim CF_2\text{-}\dot{C}NO\text{-}CF_2\sim$. The radical is stable, does not react with H_2 and O_2, but in the presence of NO decomposes at a temperature $> 200°$.

[Abstracter's note: Complete translation.]

Card 3/3

87453

S/195/60/001/002/009/010
B004/B067

11.1220

AUTHORS: Panfilov, V. N., Tsvetkov, Yu. D., Voyevodskiy, V. V.

TITLE: Detection of Hydrogen Atoms in a Dilute Hydrogen Flame by Means of epr

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 2, p. 333

TEXT: In this "Letter to the Editor", the authors report that they detected hydrogen atoms in burning mixtures of H_2 and O_2 at 3 - 20 mm Hg by means of electron paramagnetic resonance. The experiments were made immediately above the lower flash point. After heating to 550 - 600°C, H_2 and O_2 were introduced into a quartz tube through the resonator of the epr spectrometer. A doublet with a g-factor $\sim$ 2 and a splitting of $\sim$ 500 oersteds were recorded. In a stoichiometric mixture of hydrogen and oxygen, the signal power increases by the tenfold if the total pressure is reduced from 16 to 8 mm Hg. This is explained by the quicker flow of the gas mixture at lower pressure. At 8 mm Hg, the signal amplitude increases with increasing hydrogen concentration. At present, the authors

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87453

Detection of Hydrogen Atoms in a Dilute Hydrogen Flame by Means of epr

S/195/60/001/002/009/010
B004/B067

are studying the dependence of the concentration of hydrogen atoms on temperature, pressure, and the composition of the mixture. They attempt to detect other atoms and radicals. Ye. I. Kondrat'yeva and V. N. Kondrat'yev are mentioned. There are 1 figure and 4 references: 3 Soviet and 1 US.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR)

SUBMITTED: May 23, 1960

Card 2/2

88358
S/195/60/001/004/002/015
B017/B055

5.3832 (2209)

AUTHORS: Lebedev, Ya. S., Tsvetkov, Yu. D., Voyevodskiy, V. V.

TITLE: The Origin of the Compensation Effect in Recombination Reactions of Radicals in Irradiated Polymers

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 496-502

TEXT: The authors studied the rate constants of the recombination reactions of radicals in hydrocarbon polymerizates, polyvinyl chloride and various Teflon samples. Log k^0 in irradiated polymers was found to be a linear function of the activation energy E. Table 1 gives values of k^0 and E for radical recombination in various polymers. This recombination is generally observed at temperatures around the melting point of the polymer. Within the melting range, the activation energy was found to decrease with an increase in temperature. Basing on the equation $k = k_o \exp\left[-E(T)/RT\right]$, the authors calculated E and k^0 from the relations

$$E_{eff} = E - T\partial E/\partial T \quad (1) \text{ and}$$

$$k^0_{eff} = k^0 \exp(-(1/R)\partial E/\partial T) \quad (2).$$

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88358
S/195/60/001/004/002/015
B017/B055

The Origin of the Compensation Effect in Recombination Reactions of Radicals in Irradiated Polymers

The true values of k^0 for the recombination of fluoroalkyl radicals in Teflon are shown in Table 2. They are of the order of 10^{-9} - 10^{-16} cm^3/sec. The true value of E is of the order of 10-20 kcal/mole. The assumed temperature dependence of the activation energy of radical recombination in Teflon is represented graphically in Fig. 2. The anomalous values of k^0 are ascribed not only to the occurrence of phase changes on temperature increase, but also to factors due to condensation of phases. S. Z. Roginskiy and Yu. L. Khait are mentioned. There are 2 figures, 2 tables, and 14 references: 9 Soviet, 4 US, and 1 Polish.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics of the AS USSR). Institut khimicheskoy kinetiki i goreniya CO AN SSSR (Institute of Chemical Kinetics and Combustion of CO of the AS USSR)

SUBMITTED: July 27, 1960

Card 2/2

S/051/60/008/06/010/024
E201/E691

21.4000
5.3100

AUTHORS: Lebedev, Ya.S., Tsvetkov, Yu.D., and Voyevodskiy, V.V.

TITLE: The Electron Paramagnetic Resonance Spectra of Fluoroalkyl and Nitrosofluoroalkyl Radicals in Irradiated Teflon

PERIODICAL: Optika i spektroskopiya, 1960, Vol 8, Nr 6, pp 811-814 (USSR)

ABSTRACT: The authors describe their results obtained in an investigation of electron paramagnetic resonance (EPR) spectra of fluoroalkyl and nitrosofluoroalkyl radicals in irradiated teflon at temperatures up to 300°C. An EPR spectrometer with high-frequency (300 kc/s) magnetic-field modulation, described earlier (Ref 4), was used. The samples were heated by blowing hot air around them. The EPR spectrum of the fluoroalkyl radical exhibited additional hyperfine splitting of 3.5 oersted at high temperatures. This splitting was due to the interaction of the unpaired electron with fluorine atoms in the γ-position (Fig 1 shows this at 250°C). These γ-components were broadened on cooling (Fig 2) so that at room temperature they could no longer be resolved. Fig 3 shows that on further lowering of temperature to about 16°C the β-components broaden as well and finally below 0°C the hyperfine splitting due to α- and β-atoms of fluorine

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S/051/60/008/06/010/024
E201/E691

The Electron Paramagnetic Resonance Spectra of Fluoroalkyl and Nitrosofluoroalkyl Radicals in Irradiated Teflon

disappears completely. Gordy (Ref 2) reported that the EPR spectrum of fluoroalkyl radical disappeared on interaction with NO. The present authors found that simultaneously with the disappearance of the original fluoroalkyl spectra a new complex EPR spectrum appears (Fig 4). This new spectrum is ascribed to the nitrosofluoroalkyl radical and its profile at 150°C (Fig 4a) agrees with theoretical predictions (Fig 4б). Splittings in the EPR spectrum of nitrosofluoroalkyl suggest that the unpaired electron is localized mainly at the nitrogen nucleus. The paper ends with a short discussion of the results obtained and comparison with other published work. There are 5 figures and 11 references, of which 3 are Soviet and 8 English.

SUBMITTED: September 21, 1959

Card 2/2

24,7900
5.5310

28976
S/192/61/002/005/003/005
D202/D304

AUTHORS: Lebedev, Ya.S. and Tsvetkov, Yu.D.

TITLE: Electronic paramagnetic resonance spectra of radicals formed by irradiation of polypropylene

PERIODICAL: Zhurnal strukturnoy khimii, v.2, no.5, 1961, 607-609

TEXT: The authors give results of their study of free radicals found in poly-propylene (PP) by irradiation with γ-rays of Co^{60} or by the action of high-speed electrons, but do not describe the methods used. In their experiments, they used powdered ПП (PP) samples, crystallized to various extents, the corresponding electronic paramagnetic resonance spectra ЭПР (EPR) being studied in different temperature conditions: at 77° K, at -78° C, at 25° C after defreezing in vacuo and at 40-60° C. The EPR of PP in the temperature range 77 - 195° K has

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Electronic paramagnetic ...

been studied previously. When the sample temperature is raised to 25°C the spectrum is changed, and consists of 15 lines which remain in the same position when the temperature is lowered again, although line broadening occurs; the radical content increasing with progressive crystallization. The authors assume that the 15 line spectrum consists of two superimposed spectra of 9 and 6 components with superfine structure, having the same splitting (~ 20 oer). Both spectra disappear at 40 - 60°C at equal rates. A further spectrum change is observed after 2 hours, in vacuo, at room temperature: the signal intensity gradually falling and a broad line (~ 40 oer) appaering in the center. By passing oxygen through the sample at room temperature, a peroxide line is obtained, but no effects are apparent if the oxygen is passed in after a few days. At least 4 different free radicals are believed to be present in spectra of the irradiated PP samples; after defreezing only the

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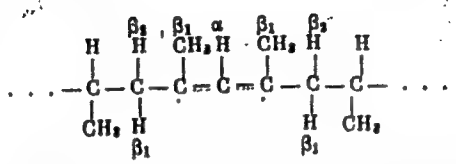
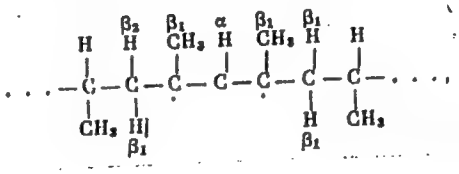
Electronic paramagnetic ...

allyl radical



R_2 has to be taken into account. Assuming that the spin density on the central C atom is small the splitting has to be observed on 8 β, protons, giving a spectrum of 9 components; the β_2 protons being oriented in such a way that they cannot take part in it. The spectrum with an even number of lines may be explained by a small admixture of the radical R_3



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Electronic paramagnetic ...

and the appearance of a broad line after prolonged standing in vacuo as the formation of some unknown radicals, more stable, than the allyl. The authors also investigated oriented PP films; when the magnetic field was oriented along the macromolecular axes, the PP spectrum was similar to that of crystalline samples; when the direction of the field formed an angle (α) with this axis, the line width became larger, reaching a maximum at $\theta = \pi/2$, but their number and position did not change. This angular EPR spectrum dependence is considered to be in agreement with the structure of the free allyl radical proposed in Western literature. The authors state that in 1961, when their paper was being printed, similar work was published in the West, the experimental results being the same, but being given a different interpretation. There are 1 figure and 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. [Abstracter's note: 1 Soviet-bloc reference is a translation from Western literature].

Card 4/5

The references to the English-language publications read as follows: S. Ohnishi, M. Kashiwagi, J. Ikeda, N. Nitta, Isotopes and Radiazion (Japan), 1,210 (1958); H. Fisher, K.H. Hellwege, V. International Simposium on Free Radicals, Uppsala (Sweden), (1961).

ASSOCIATION: Institut khimicheskoy fiziki AN USSR. Institut khimicheskoy kinetiki i goreniya CO AN USSR (Institute of Chemical Physics AS USSR. Institute of Chemical Kinetics and CO Combustion AS USSR)

SUBMITTED: April 8, 1961

Card 5/5

23770
S/190/61/003/006/013/019
B110/B208

11.2214 also 2209

AUTHORS: Tsvetkov, Yu. D., Lebedev, Ya. S., Voyevodskiy, V. V.

TITLE: Study of free radical reactions. III. Recombination of fluoroalkyl and peroxide radicals

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 882-890

TEXT: The purpose of the present paper is the investigation of the recombination reactions of fluoroalkyl and peroxide radicals under exclusion of oxygen diffusion. The dependence of the radical recombination on the ratio of the amorphous and crystalline phase was studied on Teflon with different degree of crystallinity. Teflon samples in the form of films or chips were irradiated by a γCo^{60} radiation source at ~60 Mrad. The free radical concentration is in this case $\sim 10^{18}$ $1/cm^3$. Polymerization took place on the oil bath, the electron paramagnetic resonance was studied at 10°C to determine the free radicals.

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Study of free radical reactions.
III. Recombination of ...

S/190/61/003/006/013/019
B110/B208

The kinetics of the recombination of the radicals $\dot{R}$ and $\dot{R}O_2$ was determined at different temperatures and degrees of crystallinity (74 and 46 %) (Fig. 1). The relative concentration I was referred to the initial concentration = 1: $I_\alpha = [\dot{R}O_2]/[\dot{R}O_2]_o +, I_\beta = [R]/[R]_o$. The reciprocal concentration as a function of time (Fig. 1) approaches linearity asymptotically corresponding to the bimolecular recombination reaction. In polymers with crystalline and amorphous phases (polyethylene, polypropylene, Teflon) recombination proceeds according to the bimolecular law with different rates in the amorphous and crystalline phase. Assuming that $[\dot{R}]_{cryst} = c_1$; $[\dot{R}]_{am} = c_2$ in the case of Teflon, the mean concentration $c_{mean} = c_1\alpha + c_2(1 - \alpha)$, where α = degree of crystallinity. c_1 and c_2 depend on the time: $\partial c_{1,2}/\partial t = -k_{1,2}c_{1,2}^2$ (2). According to $\lim_{t\to o}$ (1/I)

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Study of free radical reactions.
III. Recombination of ...

$= 1 + (1 - \alpha)k_2 t$ initially a rectilinear section appears in the coordinates reciprocal concentration-time (Fig. 1, curve 1), which corresponds to the square recombination in the amorphous zone, as well as a section corresponding to the square recombination in the crystalline zone in the case of higher t-values. According to (2) the straight line corresponding to the recombination in the crystalline phase cuts off the section $1/\alpha$ on the y-axis. The degree of crystallinity may thus be determined from the recombination kinetics. Table 1 gives the degrees of crystallinity calculated from the recombination kinetics $\dot{R}O_2$ and $\dot{R}$, and the α-values calculated from the specific weight (according to $d = 2.00 + 0.31\alpha\ [g/cm^3]$). Their agreement confirms the model suggested and the equality of the initial combination in both phases. The different stability of the radicals in amorphous and crystalline phase is confirmed by their decrease in concentration by 25-50 % during

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S/190/61/003/006/013/019
B110/B208

Study of free radical reactions.
III. Recombination of ...

primary heating of the irradiated samples to 150-200°C, and constancy of the concentration of repeated heating. According to (2), the rate constants of the recombination reactions at different temperatures and degrees of crystallinity can be determined from the linear anamorphisms of the kinetic curves of the type of Figs. 1, a and 5. The recombination of fluoroalkyl radicals takes place in a measurable rate only at temperatures which are by 50-70°C higher than in the case of peroxide radicals. The following is written: peroxide radicals:

$$k_{kr}^{(46)} \simeq 10^{-8} \cdot \exp\left\{-\frac{20\,000 \pm 3\,000}{RT}\right\}; \qquad (A)$$

$$k_{at}^{(46)} \simeq 10^{-16} \cdot \exp\left\{-\frac{12\,000 \pm 2\,000}{RT}\right\}.$$

fluoroalkyl radicals: $k_{kr}^{(46)} \simeq 10^{-3} \cdot \exp\left\{-(40,000 \pm 4,000)/RT\right\}$

$k_{at}^{(46)} \simeq 10^{-7} \cdot \exp\left\{-(30,000 \pm 3,000)/RT\right\}$.

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23770
S/190/61/003/006/013/019
B110/B208

Study of free radical reactions.
III. Recombination of ...

The activation energy of peroxide radical recombination is 26±3 kcal/mole in the crystalline phase, 11±3 kcal/mole in the amorphous phase. Values of 20 - 40 kcal/mole are obtained for primary alkyl radicals in various hydrocarbon polymers. The recombination of long-life radicals of solid polymers is not determined by their structure but by the properties of the medium: movement of the segments of polymer chains. In the amorphous phase with high chain mobility the recombination rate is determined by rotation of small chain parts. In the crystalline phase with firmly bound chains it is determined by the rotation of long chain parts. In the recombination rate of fluoroalkyl radicals the high values of the pre-exponential factors are remarkable, which have also been observed in other polymers (Table 2). The activation energy and the pre-exponential factor highly differ for various Teflon samples, which was also observable in many reactions of the solid phase and of the electric conductivity. The linear dependence log k^c (E) existing in this case is called compensation dependence (Fig. 3). The potential barrier of the segment rotation of the polymer chain probably decreases with a rise in temperature, which

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Study of free radical reactions.
III. Recombination of ...

explains the compensation dependence and the high pre-exponential factors, whose real values are 10^{-8} and 10^{-16} cm^3/sec. The high values obtained experimentally are thus a result of the change in activation energy with temperature rise. The authors thank G. G. Titova for her assistance in some experiments. There are 3 figures, 2 tables, and 13 references: 8 Soviet-bloc and 4 non-Soviet-bloc. The most important references to English-language publications read as follows: Ref. 4: S. Ohnishi, I. Nitta, J. Polymer Sci., 38, 451, 1959. Ref. 5: Z. Kuri, H. Ueda, S. Shida, J. Chem. Phys., 32, 371, 1960. Ref. 7: J. A. Sauer, A. E. Woodward, Rev. Mod. Phys., 32, 88, 1960.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics AS USSR).
Institut khimicheskoy kinetiki i goreniya CO AN SSSR (Institute of Chemical Kinetics and Combustion of the Siberian Division AS USSR)

LEBEDEV, Ya.S.; TSVETKOV, Yu.D.; ZHIDOMIROV, G.M.

Analysis of asymmetrical lines in electron paramagnetic resonance spectra as a method of studying internal movements in polymers. Zhur.strukt.khim. 3 no.1:21-27 Ja-F '62. (MIRA 15:3)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.
(Polymers—Spectra)

S/192/62/003/005/001/003
D267/D308

AUTHORS: Zhidomirov, G.M., Lebedev, Ya.S. and Tsvetkov, Yu.D.

TITLE: Form of line in the electronic paramagnetic resonance spectra of peroxide type radicals in oriented polymers

PERIODICAL: Zhurnal strukturnoy khimii, v. 3, no. 5, 1962, 541-545

TEXT: It was shown in an earlier paper that the spectrum of peroxide radicals ($RO_2^{\cdot}$) in oriented specimens depends on the orientation of the specimen in the magnetic field. To calculate the line form in the e.p.r. spectrum for oriented specimens the authors assumed that (1) the peroxide radical has an axial symmetry of the g factor and (2) the symmetry axes of this factor are distributed randomly in the plane S at right angles to the orientation direction of polymer chains. The calculation has been carried out to the end for the case of an infinitely narrow individual line, when the external magnetic field is parallel to the orientation axis. It has

Card 1/2

Form of line ...

been shown that the form of the e.p.r. line can be used for determining the degree of orientation of the chains (such estimation has been carried out for a Teflon specimen oriented by stretching). The paper ends with a discussion of the structure of peroxide type radicals (on the strength of the data showing the temperature dependence of the form of e.p.r. lines). There are 3 figures.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya SO AN Novosibirsk SSSR (Institute of Chemical Kinetics and Combustion, Siberian Branch of the AS Novosibirsk, USSR); Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, AS USSR)

SUBMITTED: June 17, 1961

Card 2/2

LEBEDEV, Ya.S.; TSVETKOV, Yu.D.; VOYEVODSKIY, V.V.

Free radical reactions in irradiated polytetrafluoroethylene. Part 4: Reactions of fluoroalkyl radicals with molecules from the gaseous phase. Vysokom. soed. 5 no.10:1500-1506 O '63. (MIRA 17:1)

1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.

LEBEDEV, Ya.S.; TSVETKOV, Yu.D.; VOYEVODSKIY, V.V.

Free radical reactions in irradiated polytetrafluoroethylene. Part 5: Discussion of the reaction mechanism. Vysokom.soed. 5 no.11:1608-1614 N '63. (MIRA 17:1)

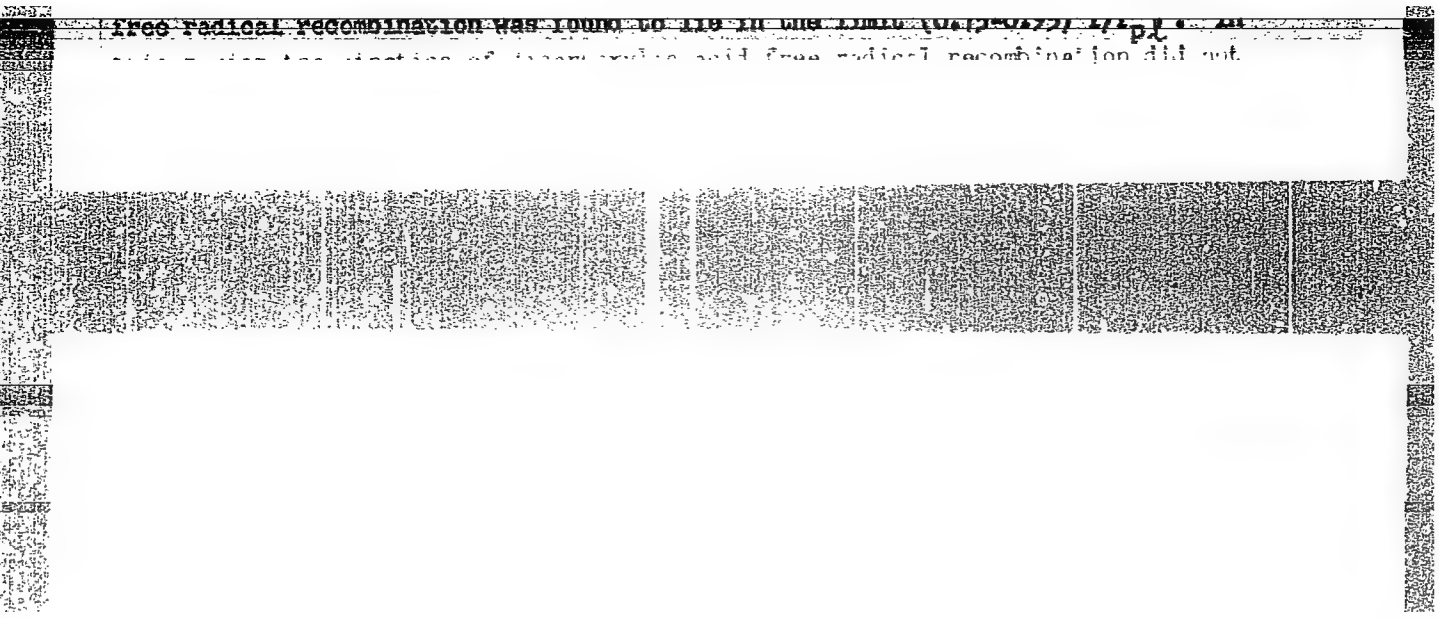
1. Institut khimicheskoy fiziki AN SSSR i Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.

ZHIDOMIROV, G.M.; TSVETKOV, Yu.D.

Use of the electron paramagnetic resonance method in studying conformations of free radicals in some alicyclic compounds. Opt. i spektr. 17 no.1:67-72 Jl '64. (MIRA 17:9)

35

by means of electron paramagnetic resonance (EPR)



helping in the experiments. Orig. art. has: 2 figures, 1 table, and 2 formulas.

TSVETKOV, Yu.D.; FALALEYEV, O.V.

Electron paramagnetic resonance study of the recombination of stable radicals in irradiated organic single crystals. Kin.i kat. 5 no.6:1119-1120 N-D '64. (MIRA 18:3)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova, khimicheskiy fakul'tet i Institut khimicheskoy fiziki AN SSSR.

ACC NR: AP7001221 SOURCE CODE: UR/0066/66/000/012/0015/0017

AUTHOR: Tsvetkov, Yu. N.

ORG: SKB of the Semiconductor Institute, AN SSSR (SKB Institut poluprovodnikov AN SSSR)

TITLE: Air-conditioning thermopile

SOURCE: Kholodil'naya tekhnika, no. 12, 1966, 15-17

TOPIC TAGS: thermoelectric equipment, thermoelectric cooling, air conditioning equipment

ABSTRACT: Vibration- and impact-resistant air-conditioning thermopile was developed and tested in 1965 at the Semiconductor Institute. It consists of 96 series-connected thermocouples which assure high reliability. The thermopile carrier consists of a 244 x 100 x 20 mm copper plate with drilled channels for the circulating cooling water. On both sides of the plate, thermocouple units, are fixed with wood solder. These units consist of two 33.5 x 12.0 x 5.0 mm corrugated heat transmitters electrically insulated with teflon, a 1.5-mm thick common copper commutation plate, and four lead-lined thermocouples. The 33 x 5.5 x 4.0 mm thermocouple arms are made from a triple alloy, and are plated on both sides with a BiSb alloy. To these arms 0.5-mm thick lead plates are soldered; these serve as dampers of thermal stresses arising in the thermocouples. On the cold side of the thermopile are placed copper

Card 1/2 UDC: 621.565.83:628.83

ACC NR: AP7001221

ribs 0.5 mm thick and 30 mm high spaced 1.5 mm apart. They are protected from mechanical damage by two vinyl coatings. The thermopile efficiency is 200.0 kcal/hr for cooling and 280 kcal/hr for heating. If the temperature of the cooling water is lowered from 30 C to 10 C, the efficiency of cooling operation increases to 400 kcal/hr. Orig. art. has: 4 figures and 1 table. [JP]

SUB CODE: 13, 20/ SUBM DATE: none/ ATD PRESS: 5110

Card 2/2

TSVETKOV, Yu.V.; BASIYEVA, N.Ya.

Behavior of tin and mercury impurities during the vacuum distillation of selenium. Zhur.neorg.khim. 6 no.10:2374-2379 O '61. (MIRA 14:9)

1. Institut metallurgii imeni A.A.Baykova AN SSSR.
(Selenium) (Tin) (Mercury)

TSVETKOV, Yu.V.

Autocatalytic phenomena in reactions involving solids. Kin.i kat. 2 no.6:827-829 N-D '61. (MIRA 14:12)

1. Institut metallurgii imeni Baykova AN SSSR.
(Catalysis) (Solids)

CHIZHIKOV, D.M.; TSVETKOV, Yu.V.; EDEL'SHTEYN, V.M.

Study of the liquid - vapro equilibrium in high-boiling mixtures under pressures distinct from the atmospheric pressure, as exemplified by the cadmium - zinc system. Dokl. AN SSSR 143 no.3: 655-657 Mr '62. (MIRA 15:3)

1. Chlen-korrespondent AN SSSR (for Chizhikov).
(Cadmium-zinc alloys)(Phase rule and equilibrium)

TSVETKOV, Yu.V.; CHIZHIKOV, D.M.

Kinetics of the simultaneous reduction of lead and zinc oxides by means of carbon oxide. Trudy Inst. met. no.4:84-88 '60. (MIRA 14:5)

(Lead—Metallurgy)
(Zinc—Metallurgy)

S/076/62/036/012/013/014
B101/B180

AUTHORS: Tsvetkov, Yu.V., Edel'shteyn, V. M., and Tagirov, I. K. (Moscow)

TITLE: Method of studying the liquid - vapor equilibrium of high-boiling mixtures at pressures other than atmospheric

PERIODICAL: Zhurnal fizicheskoy khimii, v. 36, no. 12, 1962, 2806 - 2808

TEXT: An apparatus with vapor recirculation based on one by J. Othmer (Ind. Eng. Chem., 20, 743, 1928) is suggested for determining the liquid - vapor equilibrium of high-boiling alloys. 2500 g of the alloy are heated in an evaporator at constant temperature. The temperature in the steam receiver is kept just above the dew point, while in the condenser it is kept below dew point, but above boiling point. As soon as equilibrium is established, samples taken from condenser, evaporator, and recirculator are analyzed. A cadmium - zinc system was used to test this method. The liquid - vapor equilibrium diagram was plotted for alloys containing 0, 25, 50, 75, and 100 mole% Cd at pressures of 200, 760, and 2280 mm Hg (Fig. 3). There are 3 figures.

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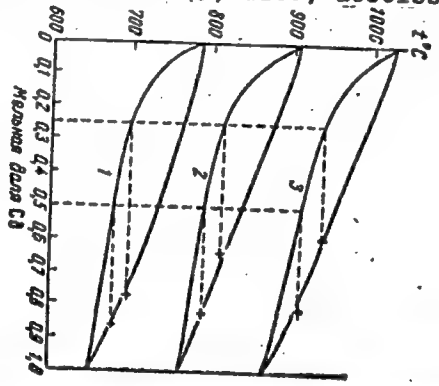
Method of studying the ...

S/076/62/036/012/013/014
B101/B180

ASSOCIATION: Institut metallurgii im. A. A. Baykova (Institute of Metallurgy imeni A. A. Baykov)

SUBMITTED: March 22, 1962

Fig. 3. Liquid - vapor equilibrium diagram in the Cd - Zn system; pressures in mm Hg : (1) 200; (2) 760; (3) 2280; abscissa : molar part of Cd.



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S/080/62/035/009/002/014
D204/D307

AUTHORS: Tsvetkov, Yu.V., and Edel'shteyn, V.M.

TITLE: The influence of pressure on the activity of components in boiling alloys of cadmium and zinc

PERIODICAL: Zhurnal prikladnoy khimii, v. 35, no. 9, 1962, 1927 - 1933

TEXT: The above problem was investigated to determine the effect of pressure on the effectiveness of separation (e.g. by distillation) of components possessing similar, high boiling points, from their mixtures. Analytical purity metals were used. The boiling points (T) of alloys containing 0, 25, 50, 60, 75 and 100 mole % Cd were measured between 100 and 3800 mm Hg and were found to range respectively from 735 to 1090, 650 to 1000, 633 to 977, 627 to 967, 623 to 957 and 610 to 930°C for the above compositions. Good linear relationships were obtained by plotting log π, where π = pressure, against 1/T (°K). The activity coefficients of Cd (γ) were calculated with the aid of van Laar's equation for molar fractions of Cd of 0.05, 0.1, 0.25, 0.4, 0.5, 0.6, 0.75, 0.9 and 0.95, between 100

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The influence of pressure on ...

and 3800 mm Hg, finding values: γ_{100} = 2.343, 2.149, 1.701, 1.405, 1.266, 1.163, 1.060, 1.009, 1.002 and γ_{3800} = 1.364, 1.322, 1.213, 1.132, 1.090, 1.056, 1.022, 1.003 and 1.001 for the above compositions respectively. These values were in fair agreement with those calculated from $\log \gamma = \frac{\Delta \bar{H}}{4.576T}$, where $\Delta \bar{H}$ is the partial heat of solution. Thus Cd-Zn systems showed positive deviations from Raoult's law, which increased at lower pressures and at higher contents of Zn. The efficiency of separation of the two components by distillation or rectification should therefore be promoted by lowering the external pressure. There are 4 figures and 3 tables.

ASSOCIATION: Institut metallurgii imeni A.A. Baykova, AN SSSR
(Institute of Metallurgy imeni A.A. Baykov, AS USSR)

SUBMITTED: June 19, 1961

CHIZHIKOV, D.M.; TSVETKOV, Yu.V.; BEREZKINA, L.G.

Effect of the crystal structure of a substance on its reduction kinetics. Kin. i kat. 2 no.1:50-54 Ja-F '61. (MIRA 14:3)

1. Institut metallurgii imeni A.A. Baykova, AN SSSR.
(Reduction, Chemical)
(Chemical reaction, Rate of)

TSVETKOV, Yu.V. , Cand Tech Sci -- (diss) "Kinetics of lead and zinc the reduction of oxides and their mixtures with carbon monoxide."

Mos, 1958, 11 pp (Acad Sci USSR. Inst of Metallurgy im A.A. Baykov) 110 copies (KL, 23-58, 108)

S/509/60/000/004/005/024
E021/E106

AUTHORS: Tsvetkov, Yu.V., and Chizhikov, D.M.

TITLE: The Kinetics of the Joint Reduction of Lead and Zinc Oxides by Carbon Monoxide

PERIODICAL: Akademiya nauk SSSR. Institut metallurgii. Trudy, No.4, 1960. Metallurgiya, metallovedeniye, fiziko-chimicheskiye metody issledovaniya, pp. 84-88

TEXT: Experiments were carried out by means of methods reported previously (Refs 1-3), on the reduction of the oxides separately, using a vacuum apparatus with continuous circulation of gases and freezing the carbon dioxide formed in the process. The final products of the experiments were subjected to phase analysis, with the assistance of B.Ya. Tratsevitskaya. Molar mixtures of oxides in the following ratios were used: PbO:ZnO 1:6, 1:3, 1:1 and 3:1. Experiments were carried out with pressures of carbon monoxide of 25 and 100 mm mercury and temperatures of 600, 700 and 800 °C. Preliminary experiments had shown that no compounds were formed in this region. A small addition of lead oxide had no marked effect on the kinetics of the

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S/509/60/000/004/005/024
E021/E106

The Kinetics of the Joint Reduction of Lead and Zinc Oxides by Carbon Monoxide

reduction of zinc oxide. As the lead oxide content increased, the reduction of zinc oxide was retarded. This effect was less marked at higher temperatures, with higher carbon monoxide pressure and with greater degree of reduction of lead oxide in the mixture. The reason for the observed phenomenon was thought to be a local increase in concentration of carbon dioxide formed during the reduction of lead oxide. The carbon dioxide was adsorbed on the active centres of the zinc oxide surface, preventing adsorption of the reducing gas and thus retarding the process. At 800 °C, the volatility of metallic lead during reduction of the mixture was higher than that observed during reduction of the separate oxide. The volatility increased with increase in relative content of zinc oxide in the mixture.
There are 4 figures, 1 table and 4 Soviet references.

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TSVETKOV, Yu.V.; CHIZHIKOV, D.M.

Kinetics of the reduction of zinc oxide by carbon monoxide. Trudy Inst. met. no.3:171-180 '58. (MIRA 12:3)
(Zinc oxide) (Oxidation-reduction reaction)

GVELESIANI, G.G. (Moscow); KONYSHKOVA, T.Ye. (Moscow); TSVETKOV, Yu.V. (Moskow); CHIZHIKOV, D.M. (Moscow)

Theory of the reduction of heavy nonferrous metal oxides and their mixtures by carbon monoxide. Izv.AN SSSR. Otd.tekh.nauk no.8:19-25 Ag '58. (MIRA 11:9)
(Reduction, Chemical) (Metallic oxides) (Carbon monoxide)

TSVETKOV, YU. V.

18(4) PHASE I BOOK EXPLOITATION SOV/1896

Akademiya nauk SSSR. Institut metallurgii

Metallurgiya, metallovedeniye, fiziko-khimicheskiye metody issledovaniya (Metallurgy, Study of Metals, and Physicochemical Methods of Investigation) Moscow, Izd-vo AN SSSR, 308 p. (Series: Its: Trudy, vyp. 3) Errata slip inserted. 3,000 copies printed.

Resp. Ed.: I.P. Bardin, Academician; Ed. of Publishing House: A.N. Chernov; Tech. Ed.: I.F. Kuzmin.

PURPOSE: This book is of interest to researchers in metallurgy, as well as to the technical personnel of the metallurgical industry.

COVERAGE: This volume of the Trudy (Transactions) of the Institut metallurgii imeni A.A. Baykova (Metallurgical Institute im. A.A. Baykov) contains 31 studies on metallurgy, individual metals and alloys, and physicochemical methods of investigation. Some of the studies pertain to the reduction of titanomagnetites, the viscosity and other characteristics of blast furnace slag, dislocation in metals, cracking of metals due to corrosion, simultaneous

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solubility of metals at various temperatures, apparatus for measuring electrical resistance and for determining the melting point of alloys and metals, optical spectral analysis, quantitative determinations by the sublimation method, and aging of alloys. Each study is accompanied by references.

TABLE OF CONTENTS:

Metallurgy, Study of Metals (Cont.) SOV/1896

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(14)

Tsvetkov, Yu.V.

137-1958-3-4652

Translation from: Referativnyy zhurnal, Metallurgiya, 1958, Nr 3, p 27 (USSR)

AUTHORS: Tsvetkov, Yu. V., Chizhikov, D. M.

TITLE: On the Kinetics of the Reduction of an Oxide of Lead by an Oxide of Carbon (O kinetike vosstanovleniya okisi svintsa okis'yu ugleroda)

PERIODICAL: Tr. In-ta metallurgii AN SSSR, 1957, Nr 2, pp 65-67

ABSTRACT: Experiments were carried out in a vacuum installation with continuous circulation and continuous automatic regulation of the pressure of the reducing agent (CO), as well as with a trap containing N_2, in which the forming CO_2 was frozen out. Experiments showed that the reduction of PbO is detectable at 400° and at a CO pressure of 300 mm Hg. The speed of the process increases with temperature and with increasing pressure of the reducing agent. Thus, within a 10 min period at 300 mm Hg of CO pressure, and at temperatures of 500°, 600°, 700°, and 800°, the PbO is reduced by 5.6 percent, 22.3 percent, 75 percent, and 100 percent, respectively. At 700° and CO pressures (in mm Hg) of 25, 500, 100, and 300, 35 percent, 43 percent, 75 percent, and 100 percent of PbO, respectively, were reduced.

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137-1958-3-4652

On the Kinetics of the Reduction of an Oxide of Lead (cont.)

It is noted that under conditions of shaft furnace smelting of Pb, the reduction of structurally free PbO should be completed in the upper zones of the furnace.

A. P.

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CHIZHIKOV, D.M. (Moskva); VOLKOVA, M. Ye. (Moskva), TSVETKOV, Yu.V. (Moskva)

Certain physicochemical properties of melts in the system tin monoxide - silica. Izv. AN SSSR Met. i gor. delo no.3: 82-90 My-Je'64 (MIRA 17:7)